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2020 Winter Conference on Plasma Spectrochemistry - Luiza Albuquerque - Poster

Luiza Gimenes Rodrigues Albuquerque, Beau J Barker, Leah N Squires

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ASSESMENT OF IMPURITIES IN Np METAL USING DOUBLE-FOCUSING SF-ICP-MS

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Production of 99.999% pure Np metal from NpO_2 and the determination of its impurities are the main goals of this research

◊ High-purity Np is required to accurately measure its fundamental physical properties, in order to support transmutation and nuclear fuels development research.

◊ Very little Np is available in its metal form, so a process of producing Np metal from NpO_2 was recently developed at INL[1].

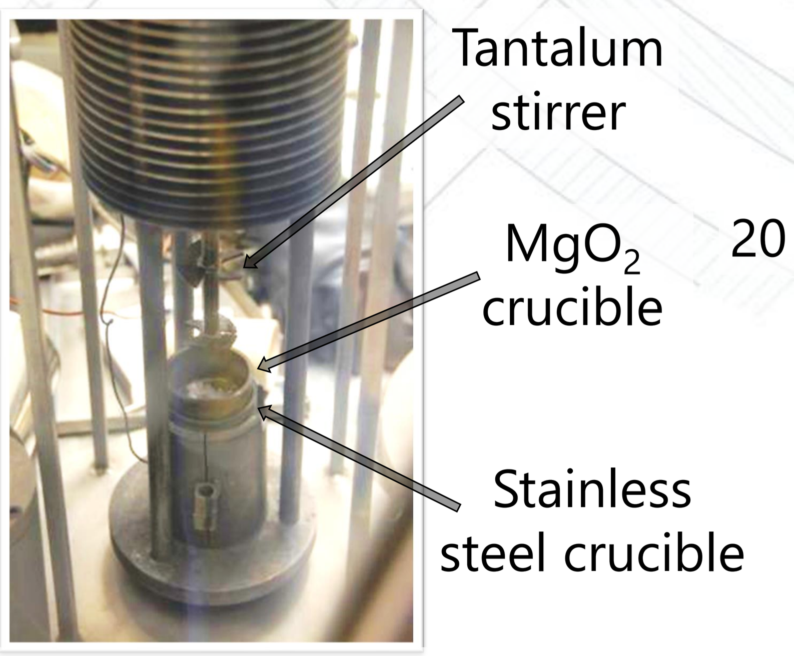
[1] Squires, L. and Lessing, P. 2016. *Journal of Nuclear Materials*, 471, pp. 65-68
[2] Richter, S. *et al.*, 2013. *Journal of Analytical Atomic Spectrometry, 28*, 10, pp. 1540-1543
[3] Becker, J. S. and Dietze, H. 2003. *International Journal of Mass Spectrometry, 228*, 2-3, pp. 127-150

Purity of the material (%) = 100% Np – Impurities[2,3]
Maximum certifiable purity = 100% Np - ∑ LOQ

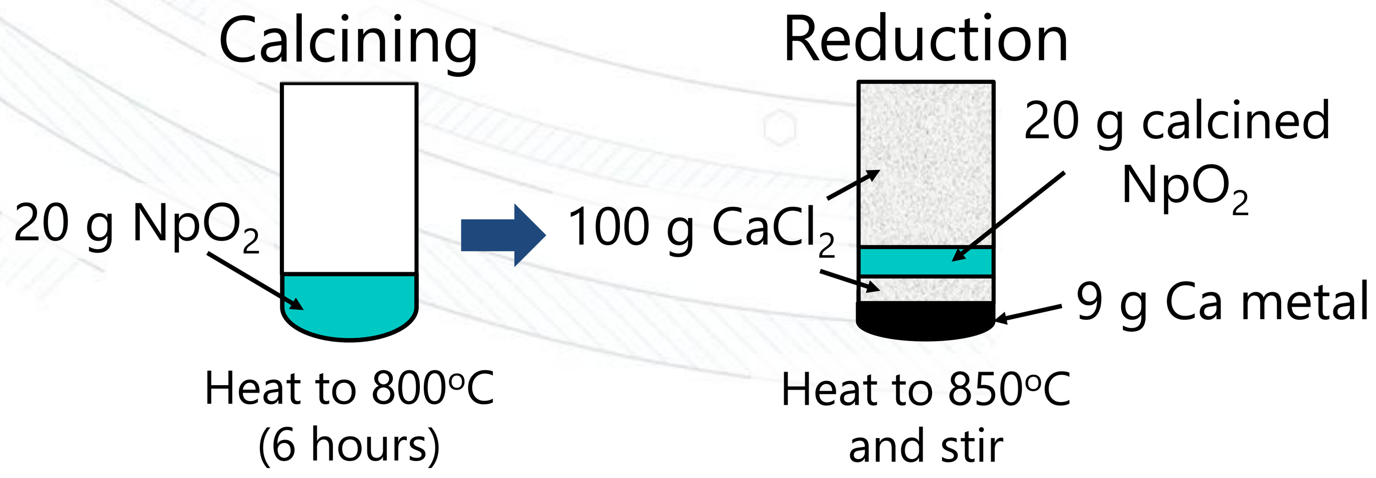
Analytical challenges:

Identify impurities and achieve low detection limits

NpO_2 reduction



Hot Uniaxial Press apparatus



$$2\,Ca + NpO_2 \rightarrow 2\,CaO + Np$$

A neptunium metal button is formed at the bottom of the reaction mixture due to its higher density

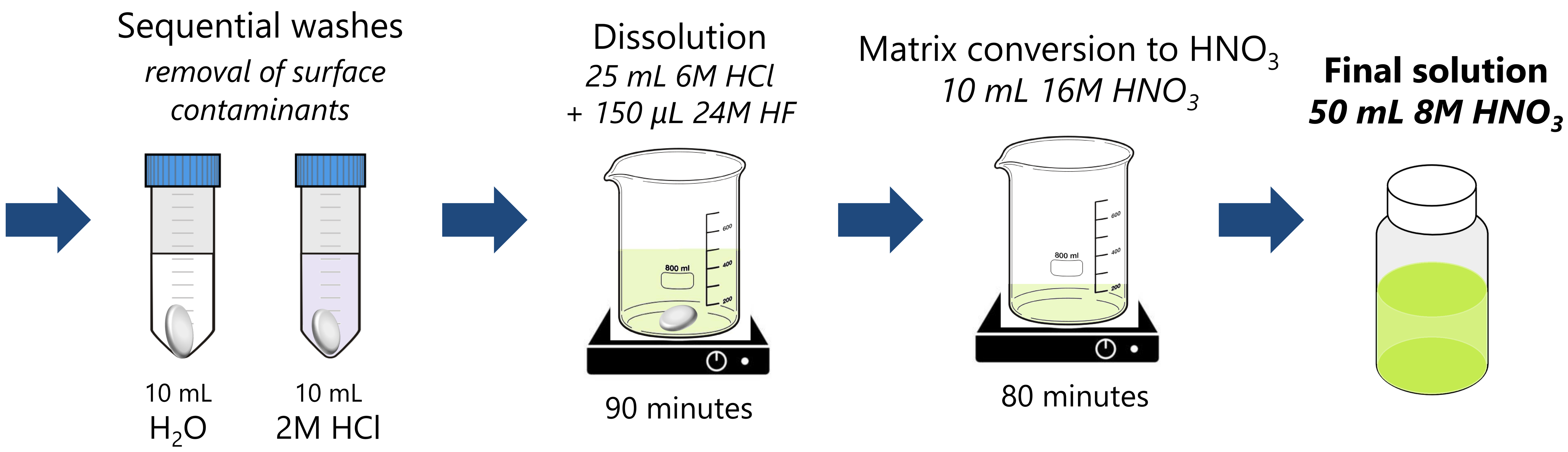
Instrumentation

Instrumental parameters	
RF Power (*W*)	1300
Ar cooling gas (*L min⁻¹*)	14
Ar auxiliary gas (*L min⁻¹*)	1
Nebulizer gas pressure (*psi*)	32
Sample uptake rate (*µL min⁻¹*)	190
Dwell time per peak (*ms*)	5
Number of sweeps	300
Resolution modes (*m/Δm*)	300 and 4000
Acquisition modes	
300 RP	Deflector jump
4000 RP	Deflector scan

Nu Instruments Attom ES HR-ICP-MS
Attached to a radiological hood

Sample dissolution

Np metal button (approx. 0.6 g)



Both washes and the dissolved sample were first evaluated by its qualitative mass scans. Elements were later quantified using Double Focusing SF-ICP-MS

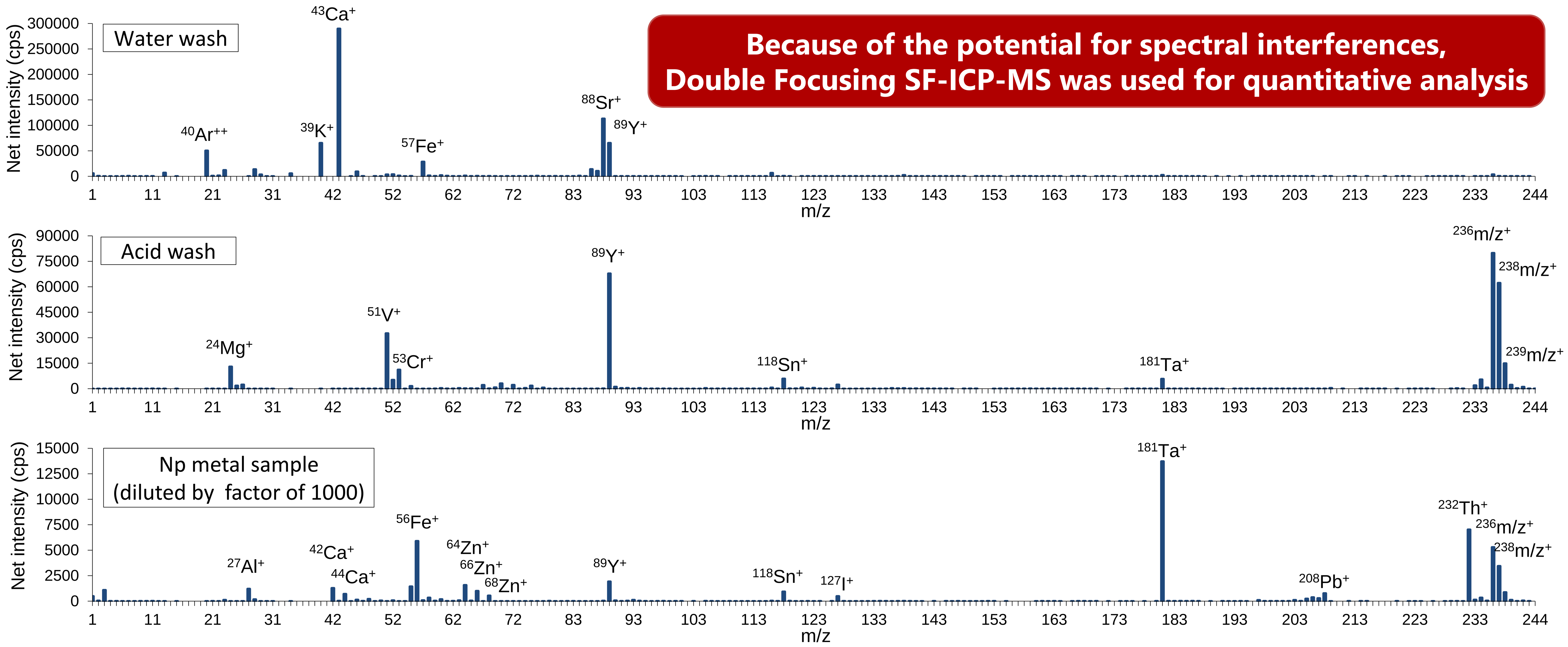
Impurities identification

○ The water wash removed mostly analytes present in the Np metal production process, indicating that they were present as surface contamination.

○ The HCl wash had a similar peak pattern to the Np metal sample, indicating that the process not only removed surface contamination, but also reacted with the sample itself.

○ Tantalum, and some actinides are the candidates for major impurities on the Np metal. Minor impurities could include Al, Au, Ca, Cr, Fe, I, Nb, Ni, Pb, Sn, Tl, Y and Zn. These contaminants can have several different origins, such as the materials used for the casting process, the use of contaminated NpO_2 as the starting material or environmental contamination.

Because of the potential for spectral interferences, Double Focusing SF-ICP-MS was used for quantitative analysis



ASSESMENT OF IMPURITIES IN Np METAL USING DOUBLE-FOCUSING SF-ICP-MS

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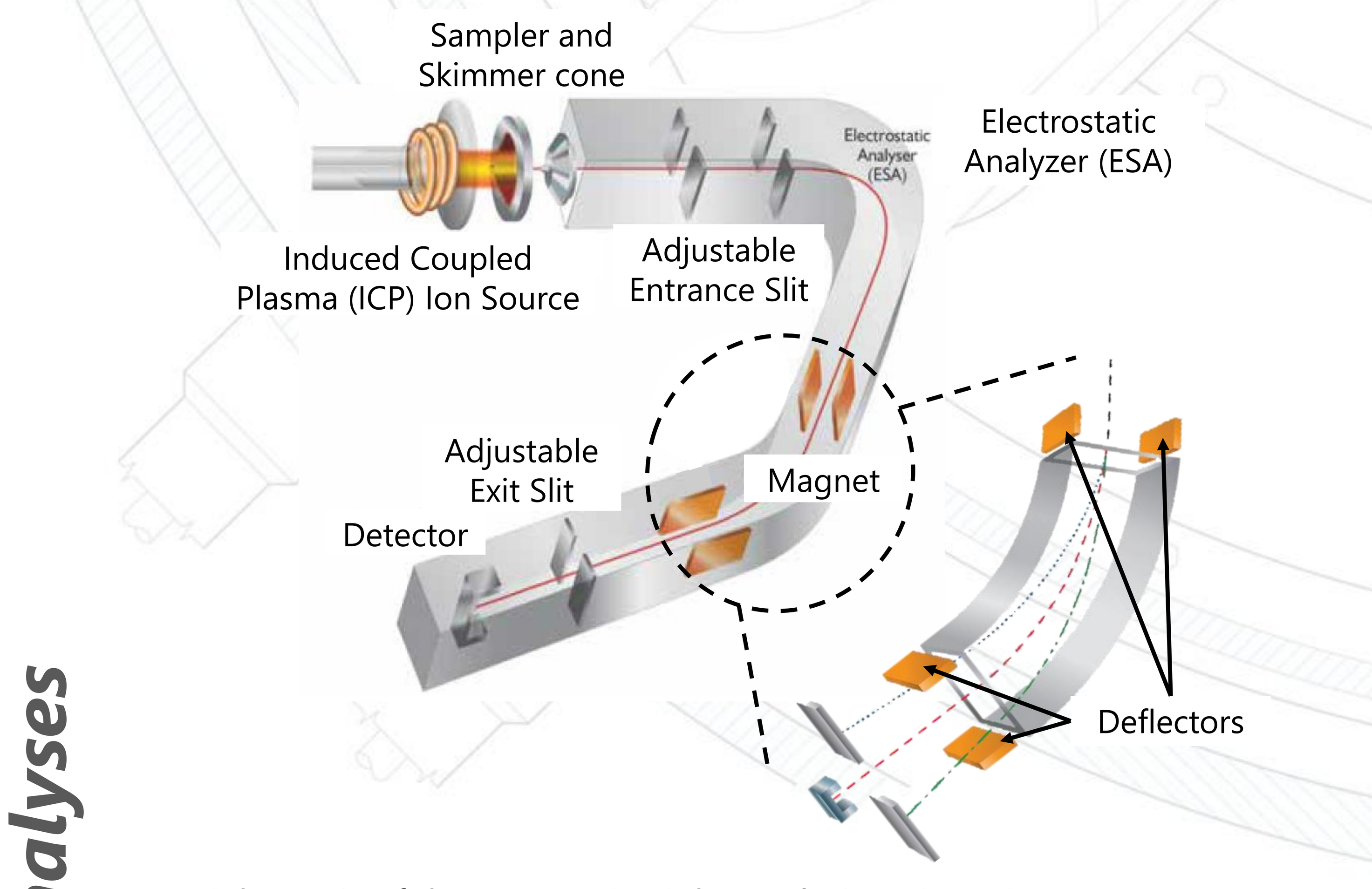
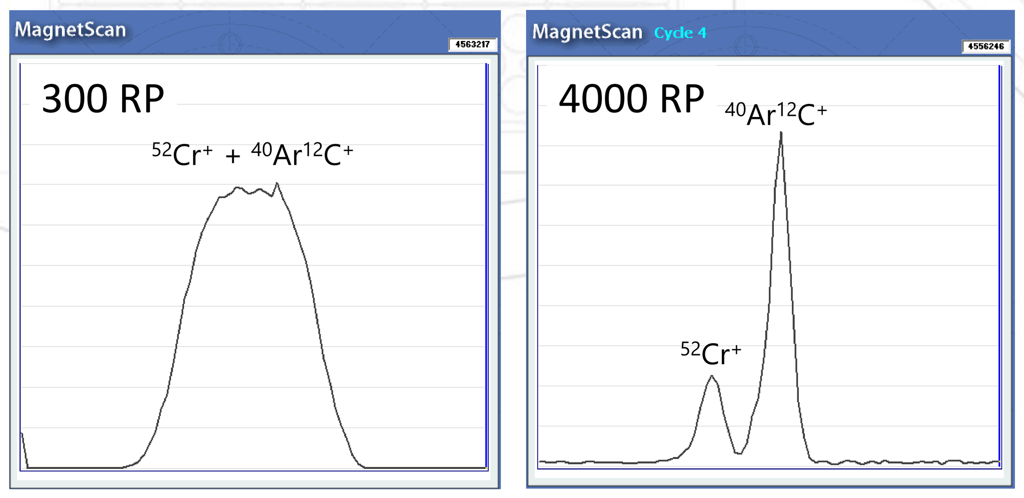
Impurities evaluation and HR-IP-MS analyses



Schematic of the Attom ES: High Resolution ICP-MS (*Nu Instruments*)

- Double-focusing instrument – ESA focuses the energy of the ions coming from the entrance slit, and magnet focuses the ions related to their m/z onto the exit slit
- Deflectors voltage can be changed for each "parked mass" of the magnet – faster analysis over a wide mass range
- Adjustable entrance and exit slits are used to set the Resolving Power (RP), varying from 300RP to 10000RP
- A narrower slit increases the RP, but decreases sensitivity due to attenuation of the ion beam



Mass spectrum of a 0.2 ng g^{-1} Cr solution

For each isotope analyzed, several items were evaluated:

- Raw signal for 5% HNO_3 (rinse) and sample preparation blanks
- Determination coefficient and sensitivity of calibration curves
- Possibility of interferences
- Comparison of results obtained using various RP
- Limit of Quantification (LOQ)

$$LOQ = 15 * \frac{SD\ of\ 10\ measurements\ of\ the\ blank}{Slope} * sample\ dilution\ factor$$

Example: $^{52}Cr^+$ evaluation in Np samples

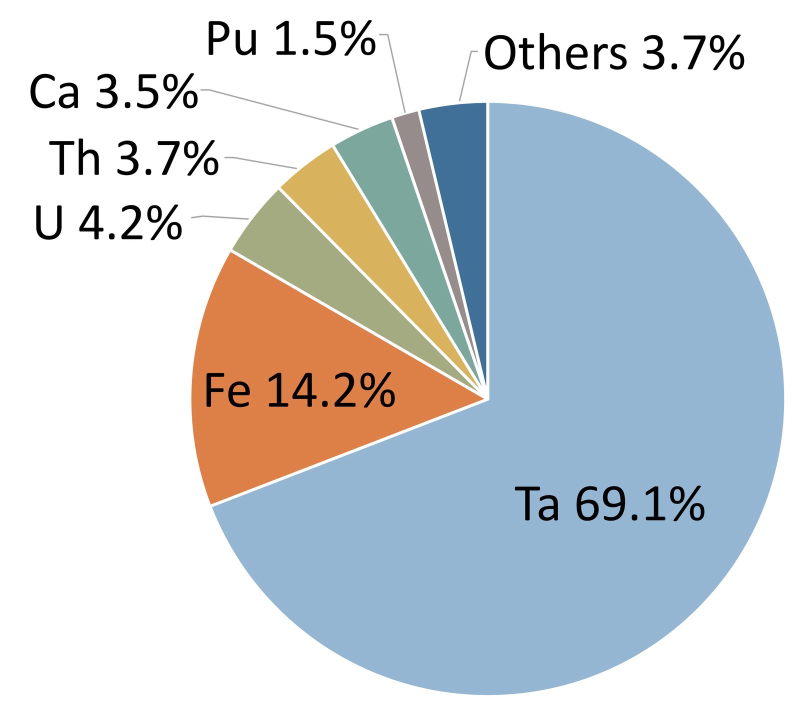
Resolving Power	*300*	*4000*	
5% HNO_3 signal intensity (*cps*)	369000	1820	Background signal reduction of over 2 orders of magnitude *Interference from $^{40}Ar^{12}C^+$ resolved*
Calibration slope	729000	121000	Sensitivity reduced by a factor of 5 *As expected, due to beam attenuation*
Calibration r^2	0.9957	0.9964	No significant change in determination coefficient
LOQ (µg g^{-1})	40	0.3	Quantification limit increased by 2 orders of magnitude *Eliminating interference compensates for sensitivity loss*
Measurement RSD (%)	5 – 20	1 – 15	Slight improvement
$^{52}Cr^+$ concentration (µg g^{-1})	<40	34.3 ± 1	^{52}Cr could be quantified using a higher RP

Element/Isotope	RP	Isotope/emission line used for total conc. calculation	Interferences	Conc. (µg/g)	RSD (%)	LOQ (µg/g)
Al	4000	^{27}Al	-	28.9	±3	3
Cr	4000	^{52}Cr	$^{36}Ar^{16}O^+$, $^{38}Ar^{14}N^+$, $^{40}Ar^{12}C^+$	41	±1	0.4
Fe	4000	^{56}Fe	$^{40}Ar^{16}O^+$	396	±2	50
I	4000	^{127}I	$^{238}U^{16}O^{++}$	<4	N/A	4
Nb	300	^{93}Nb	-	1.55	±4	0.003
Ni	300	^{60}Ni	-	19.6	±7	0.8
Pb	300	^{208}Pb	-	<0.1	N/A	0.1
Sn	4000	^{118}Sn	-	<0.2	N/A	0.2
Ta	300	^{181}Ta	-	1920	±2	0.1
Th	300	^{232}Th	-	103	±0.1	0.006
Tl	300	^{203}Tl	-	<0.001	N/A	0.001
V	4000	^{51}V	$^{14}N^{37}Cl^+$	1.68	±6	0.02
Y	300	^{89}Y	-	10.8	±1	0.005
^{233}Pa	300	^{233}Pa	-	4.56	±7	0.7
^{234}U	300	^{234}U	-	9.53	±1	0.001
^{235}U	300	^{235}U	-	2.74	±1	0.001
^{236}U	300	^{236}U	-	4.25	±5	0.5
^{238}U	300	^{238}U	-	115	±1	0.01
^{239}Pu	300	^{239}Pu	-	35.6	±1	0.002
^{240}Pu	300	^{240}Pu	-	6.05	±1	0.002
^{241}Am	300	^{241}Am	-	1.16	±7	0.002
^{242}Cm	300	^{242}Cm	-	2.55	±2	0.001
^{243}Am	300	^{243}Am	-	0.243	±5	0.001
^{244}Cm	300	^{244}Cm	-	0.0837	±4	0.001
Ca†		393.366 nm		97	±1	20

† Calcium was analyzed by ICP OES

Total impurities (µg g^{-1})	**2800 ± 2%**
Total Np purity (%)	**99.720**
Maximum certifiable purity (%, as 100% Np - ∑ LOQ)	**99.992**

- Tantalum and Fe were the main impurities, being introduced in the sample from Ta stirrer and the stainless steel crucible used in the casting process.
- Uranium, Th and Pu could have originated from an impure starting NpO_2 material.
- Calcium was also one of the contributors, originating from the Ca/$CaCl_2$ used in the reduction process



- **Np metal that was produced did not achieve the desired purity (99.999%)**
- **It was possible to identify the main sources of impurities, with great precision and accuracy**
  - The casting process will be modified accordingly to the results obtained for the main contaminants.
- **Using the current detection limits, we could certify a material with up to 99.992% purity**
  - *Detection limits can be improved - using of intermediate RP (2500).*
  - *Could also be improved by removing the Np from the solution allowing a more concentrated solution to be used and removing potential spectral interferences from the ICP OES measurements.*

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